SURFACE MODIFICATION OF TITANIUM DIOXIDE (TiO_2) THIN FILMS AND THEIR APPLICATIONS

SYNOPSIS

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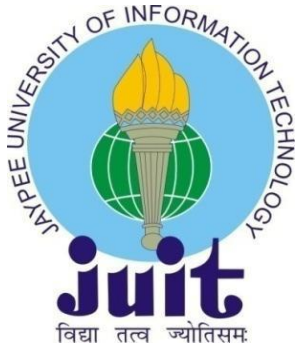

DEPARTMENT OF PHYSICS AND MATERIALS SCIENCE

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1. INTRODUCTION

Metal oxide plays a tremendously central role in the areas of physics, chemistry, materials science, biology and medical science [1, 2]. The chemical and electronic properties of metal oxide made them a stimulating candidate for technological and scientific applications. The wide band gap semiconducting oxides such as SnO_2, TiO_2, MoO_3, ZnO, Al_2O_3 etc., are useful for a number of applicationsviz. gas sensors, transparent conducting oxides and optical components. Among various materials, Titanium Dioxide (TiO_2) is one of the most investigated oxide materials in theliterature showing optoelectronics properties for variety of applications due to its biological and chemical inertness, strong oxidizing power, non-toxicity and long term stabilization against photo/chemical corrosion [3]. The TiO_2 is the only naturally occurring oxide of titanium at atmospheric pressurethat exhibits three polymorphs viz. Rutile, Anatase and Brookite. By virtue of its property as a semiconductor, when ultraviolet light is applied to TiO_2 it gives rise to electron-hole pairs that are applicable for many applications. Despite of being **a superior photo-active material the TiO_2 works only under ultraviolet irradiation (<380nm) owing to its large band gap confining its uses**. Thus, an efficient utilization of solar spectrum (mainly a good portion of the visible light) is one of the important subjects for developing future generation of TiO_2 based photo devices. However, in certain applications such as a photo-catalysts and optical absorbing material for photovoltaic cells, the band gap of TiO_2 needs to be modified to bring it into visible light range, and to generate electron–hole pairs essential for such functionalities.

TiO_2 nanomaterial also shows antifogging behavior on various glass products, i.e., eyeglasses and mirrors, having superhydrophobic or superhydrophilic surfaces [4]. Most of the applications involve surface properties of TiO_2 thin films, indicating thin film structures of TiO_2 comparatively important than other geometries in many technological applications. For the efficient utilization of TiO_2 in environmental and optical applications, its surface as well as optical properties needs to be improved. The surface modification not simply affects interfacial energy offset but also impacts considerably the charge separation, transport, recombination processes and optical properties/band gap. There is a number of ways to modify surface of a material in order to improve its functionality [5, 6] using chemical or physical techniques. They include (i) doping and deposition of TiO_2 using noble metals such as platinum [7], silver [8], gold [9] etc. (ii) inclusion of transition metals [10], (iii) and doping of non-metals [11]. Besides

these there are other approaches as well that are used to modify the band gap of TiO_2 thin film for various applications. Generally surface hydrogenation, vacuum activation and plasma treatment lays in this category. In this work, we have used a cheap method by using **air plasma** for surface modification. The used air plasma also avoids utilization of harmful gases unlike other plasma treatment methods. Thin films were formed using sol-gel method as it has many advantages than other methods for film deposition such as it provides high optical and quality films, economical, produces thick coating to provide the corrosion protection performance, low temperature, and large surface area.

2. OBJECTIVES OF THE STUDY

2.1 Objective 1:

Superhydrophilic TiO_2 thin films by surface roughness and dangling bonds

In this objective, we report effect of nanometer scale surface roughness and dangling bonds created by DC-glow discharge air plasma exposure on the superhydrophilic properties of TiO_2 thin film. The nanometer scale surface roughness and dangling bonds on the surface of film changes surface energy of liquid-vapor interface, and thus the wetting of TiO_2 film. The change in surface energy was measured via contact angle measurements using sessile drop method. To study the effect of surface roughness on wetting/hydrophilic nature of the TiO_2 films, surfaces with different roughness were produced by varying the time of plasma exposure. Each of the plasma exposed TiO_2 film was investigated for alteration in surface energy with respect to unexposed one. We observed that surface roughness along with the formation of dangling bonds makes the TiO_2 superhydrophilic. However, the contribution of surface states (formation of dangling bonds) appears up 10 second of the plasma exposure time andafterwards the surface roughness predominates.

Fabrication of TiO_2 thin films:

As stated above, we fabricated thin films by sol-gel dip coating method. 17ml of titanium precursor (Ti $(OC_3H_7)_4$) was dissolved in a mixture of 67ml of ethanol and 4.8ml of triethanolamine. Afterwards, a solution of de-ionized water (1mL) and ethanol (9mL) was added drop wise to the above solution at room temperature with continuous stirring for 2 hours. The resultant solution was cooled down to the room temperature. Then by aging for 48 hours, TiO_2 sol was formed. Next, to coat on the glass substrates the substrate were pre-cleaned ultrasonically

with acetone, ethanol and de-ionized water, and then were dipped into the solution. The withdrawing speed of dip coating was 2.5cm/min. Finally, to remove triethanolamine, coated thin films were annealed at 200^{o}C for 30 minutes [12]. Thickness of the thin films was about 350nm (as measured by profilometer). The chemical reactions involved in the synthesis process are shown in the following equations:

$$3Ti(OC_3H_7)_4 + 4N[C_2H_4OH]_3 \xrightarrow{C_2H_5OH} Ti_3[(OC_2H_4)_3N]_4 + 12C_3H_7OH \quad (1)$$

$$Ti_3[(OC_2H_4)_3N]_4 + 12H_2O \rightarrow 3Ti(OH)_3 + 4N(C_2H_4OH)_3 \quad (2)$$

Modification of films surface by plasma exposure:

Thin films were exposed in DC-glow discharge plasma with varying exposure time: 0, 5, 10, 15, 30, 60, 120 and 180 seconds. The plasma was produced using air in the discharge camber in a vacuum coating unit (Vacuum coating unit Model 12A4D). The applied voltage and discharge current were produced using DC supply. Unexposed and plasma exposed thin films were characterized by X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM) and X-ray photoelctron microscopy (XPS). The wettability transition on rough surfaces was measured by a change in contact angle of droplet of test liquids. To estimate change in surface energy of the films due to nanometer scale surface roughness by DC-glow discharge plasma, two test liquids; deionized water and ethylene glycol with known surface tension component were used (Table 1). After measuring contact angle, surface energy of unexposed and exposed TiO_2 films was calculated by following equation [13]:

$(1+\cos\theta)\gamma_{LV} = 2\,(\gamma_S^D \gamma_{LV}^D)^{1/2} + 2\,(\gamma_S^P \gamma_{Lv}^P)^{1/2}$, (3) $\gamma_S = \gamma_S^P + \gamma_S^D$ (4)

where θ is average value of apparent contact angle. The standard values of total surface tension (γ_{LV}), and its polar (γ_{LV}^P) and dispersive (γ_{LV}^D) components for water and ethylene glycol are given in Table 1 [14].

Table 1. Surface tension components of the test liquids:

Test Liquids	Polar γ_{LV}^P(mJ/m^2)	Dispersion γ_{LV}^D(mJ/m^2)	Surface tension γ_{LV} (mJ/m^2)
Deionized Water	51.0	21.80	72.8
Ethylene Glycol	19.0	29.0	48.0

Structural and Morphological studies:

XRD pattern of unexposed and plasma exposed TiO_2 thin films are presented in Figs. 1(a, b), respectively. Since the samples were annealed at 200^oC, the major peak detected at the diffraction angle (2θ) 25.3^o corresponds to the amorphous phase of TiO_2 [15]. The air plasma exposure has a negligible influence on the crystalline structure of TiO_2 thin films. For the estimation of elemental composition of the film, EDX analysis was also performed. The EDX spectrum of unexposed and plasma exposed films is shown in Figs. 2(a, b), respectively.

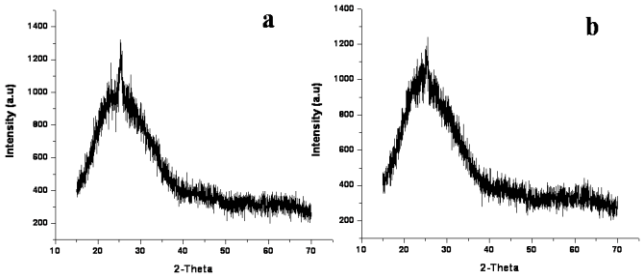

Fig.1: XRD pattern of (a) unexposed TiO_2 and (b) plasma exposedTiO_2 thin films.

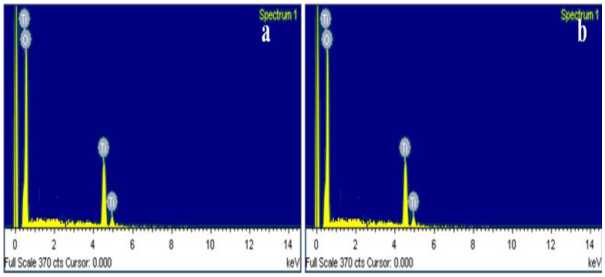

Fig.2: EDX spectra of (a) unexposed TiO_2 and (b) plasma exposed TiO_2 thin film.

Enhanced wetting properties of thin films:

The change in values of apparent contact angle with exposure time in DC-glow discharge plasma is summarized in Table 2. For unexposed TiO_2 film, the contact angle of deionized water droplet was 54.40° and that of ethylene glycol was 48.82°. After plasma exposure it reduced to 3.02^o for deionized water and 1.85^o for ethylene glycol at the surface of sample which was exposed for 180 secondsin plasma (Fig. 3.) After measuring the contact angle for different exposure time, the change in surface energy components and thus total surface energy was also calculated, which are mentioned in Table 2.

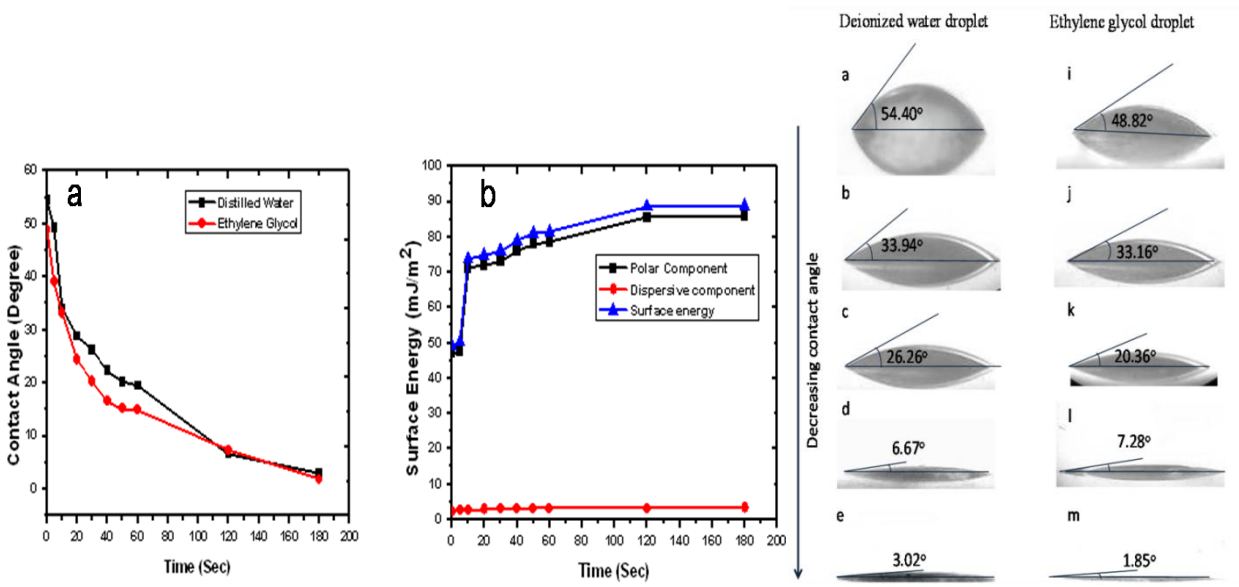

Fig.3: (Left) Variation in contact angle (a), surface energy and its polar 'γ_{LV}^{P}', dispersive 'γ_{LV}^{D}' component (b) with plasma exposure time. **(Right)** Contact angles of deionized water (a-e) and ethylene glycol (i-m) on the surface of exposed TiO_2 films exposed in plasma for different time.

Table 2. Variation of contact angle and corresponding surface energy of exposed TiO_2 films with plasma exposure time:

Time	Contact Angle (Degree)		Polar Component (mJ/m^2)	Dispersive Component (mJ/m^2)	Surface Energy (mJ/m^2)
	Deionized Water	Ethylene Glycol			
0	54.40	48.82	47.12	2.26	49.38
5	49.20	39.05	47.68	2.67	50.35
10	33.94	33.16	71.19	2.64	73.84
20	28.82	24.37	71.99	2.91	74.91
30	26.26	20.36	72.99	3.00	76.00
40	22.32	16.54	76.03	3.05	79.08
50	20.18	15.20	77.90	3.06	80.97
60	19.50	14.88	78.52	3.06	81.58
120	6.67	7.28	85.58	3.09	88.68
180	3.02	1.85	88.92	3.12	88.92

AFM and XPS studies:

To observe the variation in surface roughness produced by plasma exposure, the changes in topography of unexposed and plasma exposed TiO_2 films was analysed by AFM. The AFM images reveal a change in surface roughness upon plasma exposure. Fig. 4 represents characteristic AFM images of unexposed and plasma exposed TiO_2 films. High resolution XPS spectra of unexposed and plasma exposed TiO_2 thin films were analysed to observe variations in surface states as shown in Fig. 5. Figs. 5(a) and 5(b) corresponds to the high resolution spectra of Ti 2p peaks of unexposed and plasma exposed TiO_2 films. In case of unexposed films, the peaks were fitted as; Ti^{4+} $2p_{1/2}$ at 464.8 eV, Ti^{4+} $2p_{3/2}$ at 459.0 eV, and Ti^{3+} $2p_{3/2}$ at 460.4 eV. Similarly, three peaks in case of plasma exposed film were fitted as; Ti^{4+} $2p_{1/2}$ at 464.8, 459.1 eV for Ti^{4+} $2p_{3/2}$, and Ti^{3+} $2p_{3/2}$ at 460.4 eV. The change in stoichiometry was estimated by the change in surface area of relative peaks. In order to analyse the change in oxygen atomic states, high resolution O1s XPS spectrum was also obtained. Fig. 5(c) and 5(d) shows O1s peaks of unexposed and plasma exposed TiO_2 thin films.

Antifogging experiment:

A superhydrophilic surface can prevent fog because water spreads over the rough hydrophilic surface to form a thin film instead of droplets. Such an effect can be easily illustrated, when superhydrophilic TiO_2 thin film is exposed to hot water vapor. We observed that plasma exposed superhydrophilic TiO_2 thin film (left side image in Fig. 6) remains clear due to the formation of a continuous water film on the surface. In the right side of the Fig. 6, there is a simple glass slide that is covered by water droplets and remained fogged for several minutes. In this figure we can read the letters behind plasma exposed TiO_2 thin film easily; however, the letters behind the simple glass substrate sample without coating cannot be read clearly. These results show excellent antifogging ability of surface modified TiO_2 thin films.

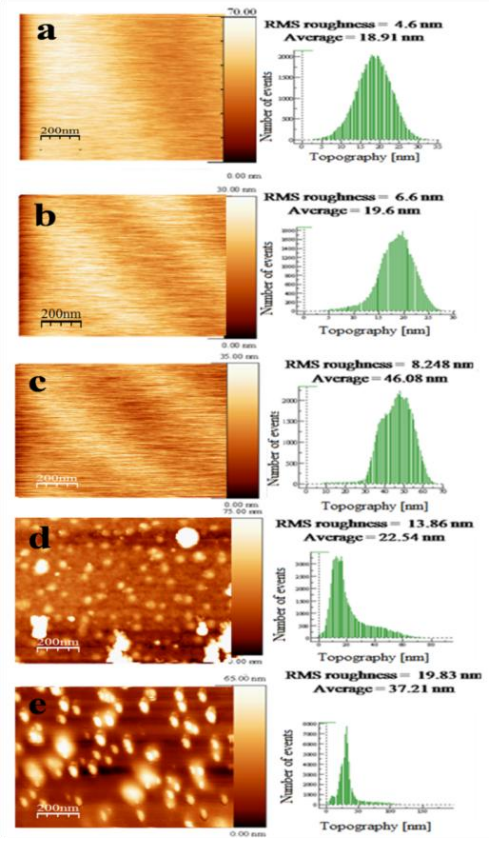

Fig.4: AFM images of unexposed andexposed TiO_2film with glow discharge plasma.

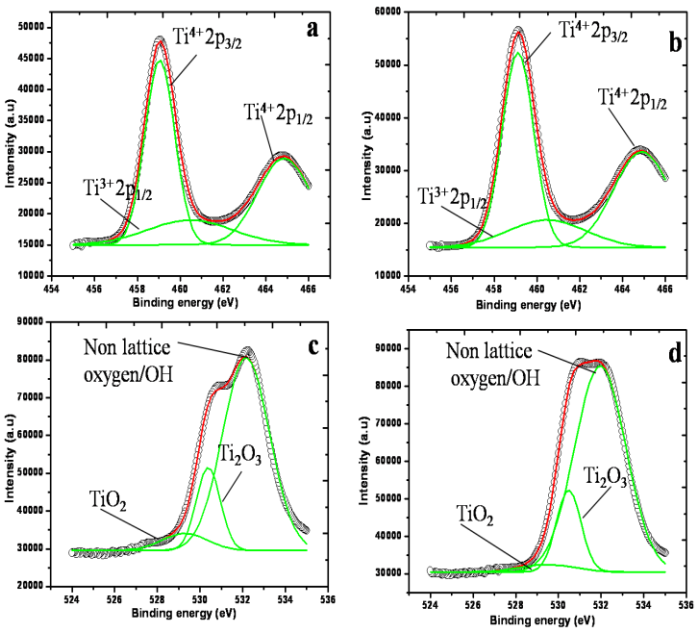

Fig.5: XPS spectra of Ti2p (a,b)and O1s (c,d) core level for TiO_2 thin films.

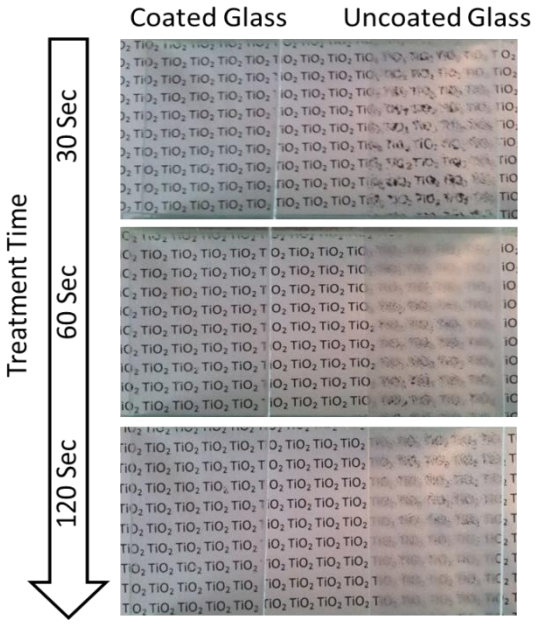

Fig.6: Comparison of antifogging properties of uncoated and TiO_2 coated glass and plasma exposed samples for (a) 30 sec, (b) 60 sec and (c) 120 sec.

2.2 OBJECTIVE 2:

Enhancement of optical properties of TiO_2 thin films as results of oxygen vacancies and Ti^{3+} states by air plasma treatment:

Band structure modification of thin transparent TiO_2 films was obtained by the air plasma exposure. The modification was contributed by the formation of Ti^{3+} and oxygen vacancies in plasma treated samples. Here, the effect of air plasma treatment was studied in conjunction with metallic doping. First, Fe and Co doped TiO_2 thin films were formed on glass substrate, which were subsequently treated in air plasma. Considering the drawback of high metallic doping, a moderate amount of dopants was used to enhance the optical properties of TiO_2 thin film and thereafter the air plasma was applied to enhance them further. The moderate amount of metallic dopant not only favors separation of electrons and holes but also narrows the band gap of TiO_2 [16]. We observed that simultaneous effect of the joint approaches increases photo absorbance as well as expends photo response region of the films towards both the visible and UV spectrum.

Experimental Method:

Pure TiO_2, Fe doped TiO_2 and Co doped TiO_2 thin films were fabricated on glass substrate using same sol-gel dipcoating method as followed in the objective 2.1. During the sol-gel synthesis, solutions of ferric nitrate (Fe $(NO_3)_3.9H_2O$), cobalt nitrate (Co $(NO_3)_2.6H_2O$) and were added separately as the dopant in TiO_2. These solutions were stirred for 2 hours and allowed for ageing overnight. Coated films were dried and annealed at 400^oC to form transparent thin films. Rest part of surface modification is similar to objective 2.1. The optical (absorbance, shift in absorption edge and band gap) properties of the films were studied by UV-Vis spectrophotometer

Structural and Morphological studies:

For structural analysis, XRD spectra of doped thin films for extreme treatment time 0 and 60 secondsare shown in Fig.7. The XRD pattern of thin films are shown in Fig. 7(a, b) and Fig. 7(c, d) for Fe doped TiO_2 and Co doped TiO_2 thin films. Fig. 8 shows SEM image of pure and doped TiO_2 thin films. Fig. 9 shows the EDX spectra of pure and doped TiO_2 thin films.

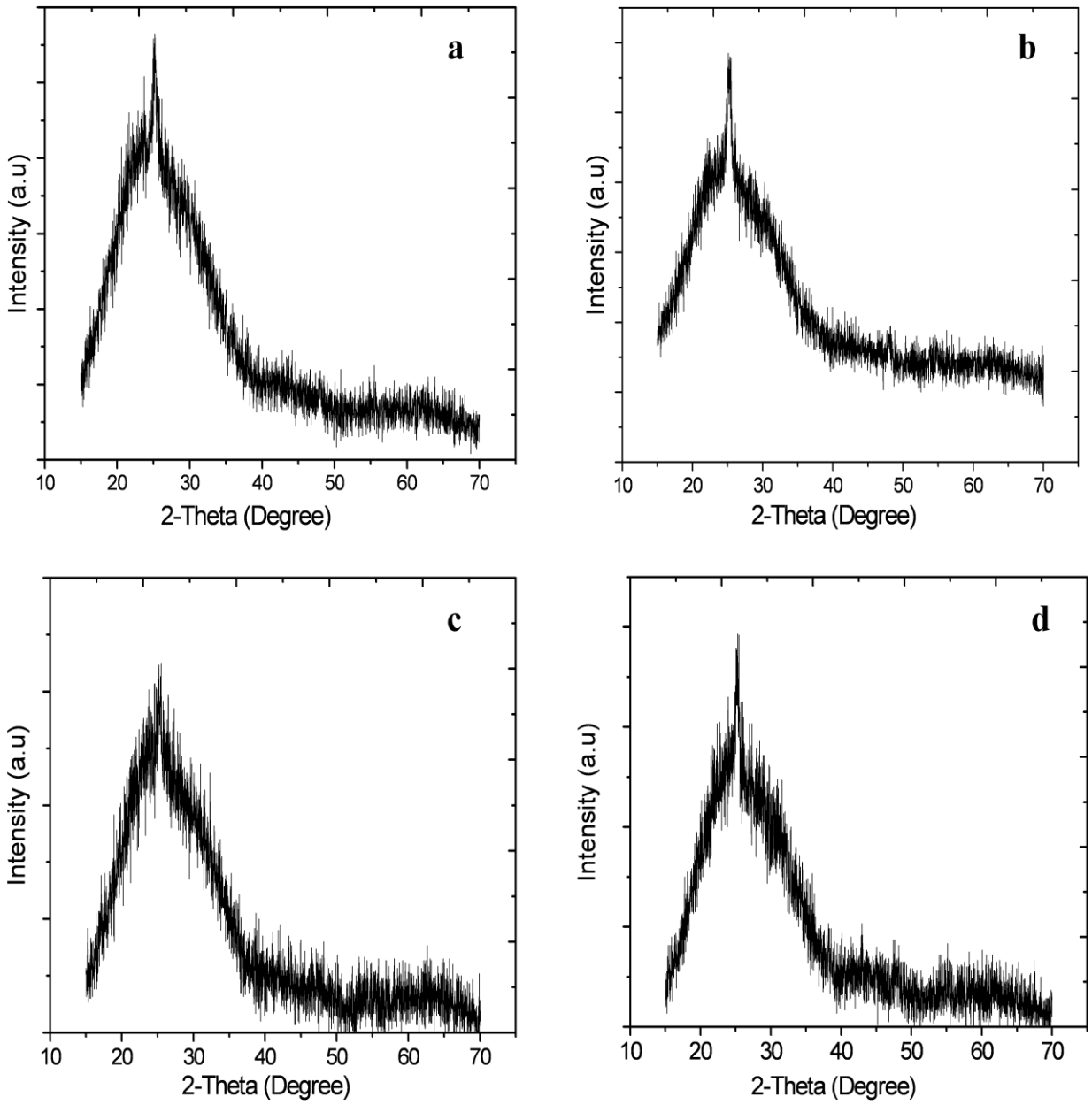

Fig.7: X-ray diffraction spectra of (a) Fe doped/untreated TiO_2 film; (b) Fe doped/treated TiO_2 film, (c) Co doped/untreated TiO_2 film, and (d) Co doped/treated TiO_2 film.

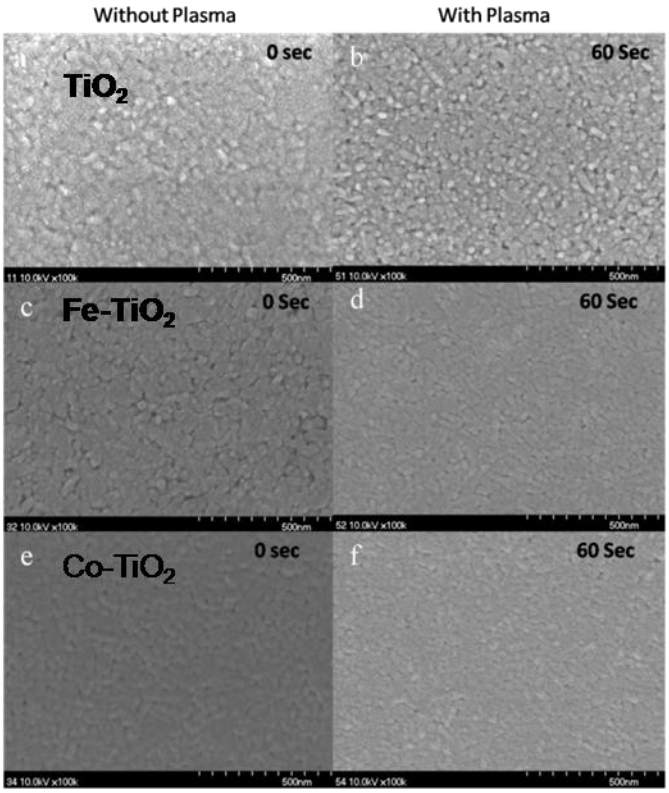

Fig.8: SEM images of TiO_2, Fe doped TiO_2 and Co doped TiO_2 thin films

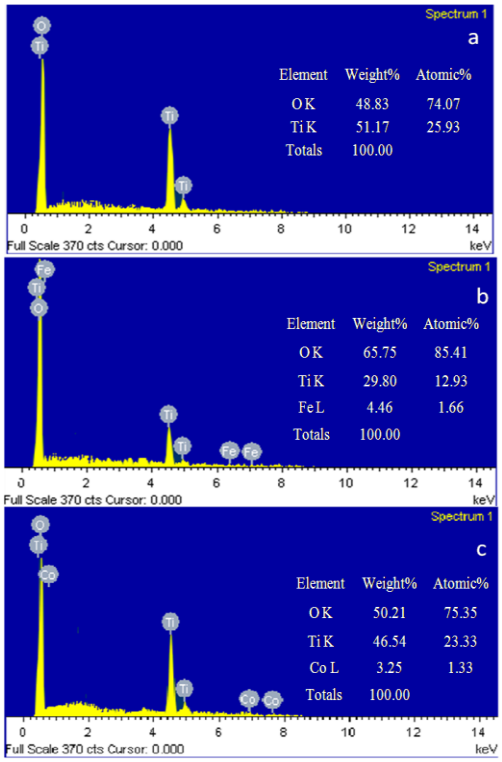

Fig.9: EDX spectrum of (a) pure TiO_2 (b) Fe doped TiO_2 and (c) Co doped TiO_2.

Optical Studies:

In order to check the variation in optical properties of TiO_2 thin films by doping and subsequent air plasma treatment the film were analyzing by UV-Vis spectrophotometer. A summary of the change in absorption edge and corresponding band gap is mentioned in Table 3. Fig. 10 shows variation in the absorption spectra of Fe doped TiO_2 thin film treated for different plasma treatment time (10, 30 and 60 seconds (Fig. 10(b-d)) with respect to untreated one (Fig. 10(a). There is a continuous change in the absorbance, absorption edge and band gap of the films with plasma treatment time.

Table 3. Variation in absorption edge and band gap of Fe and Co doped TiO_2 thin films with plasma treatment time.

Plasma treatment time [sec]	Absorption edge [nm]		Band gap [eV]	
	Fe doping	**Co doping**	**Fe doping**	**Co doping**
0	385	369	3.22	3.36 by doping
10	396	360	3.13	3.44
30	402	345	3.08	3.59 by plasma treatment
60	413	342	**3.00**	**3.62**

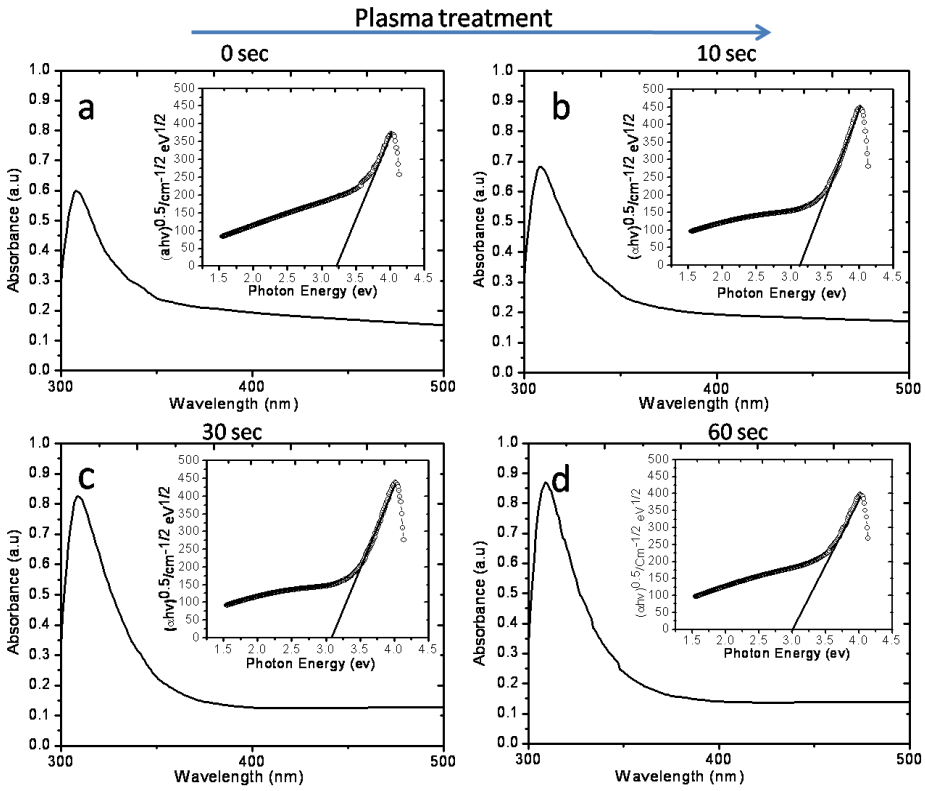

Fig.10: Optical absorption spectra and Tauc plot ($(\alpha h\nu)^{1/2}$ versus $h\nu$ plots) in the inset for (a) Fe doped/untreated TiO_2 film; plasma treatment time 0 second, (b) Fe doped/treated TiO_2 film; plasma treatment time 10 second (c) Fe doped/treated TiO_2 film; plasma treatment time 30 second and (d) Fe doped/treated TiO_2 film; plasma treatment time 60 second.

Similarly, the variation in absorption spectra of Co doped TiO_2 thin film treated for 0 to 60 seconds is shown in Fig. 11 (a-d). In this case, doping shows a red shift due to the presence of Co levels in the energy gap of TiO_2, whereas after plasma treatment the film shows continuous blue shift with increasing treatment time.

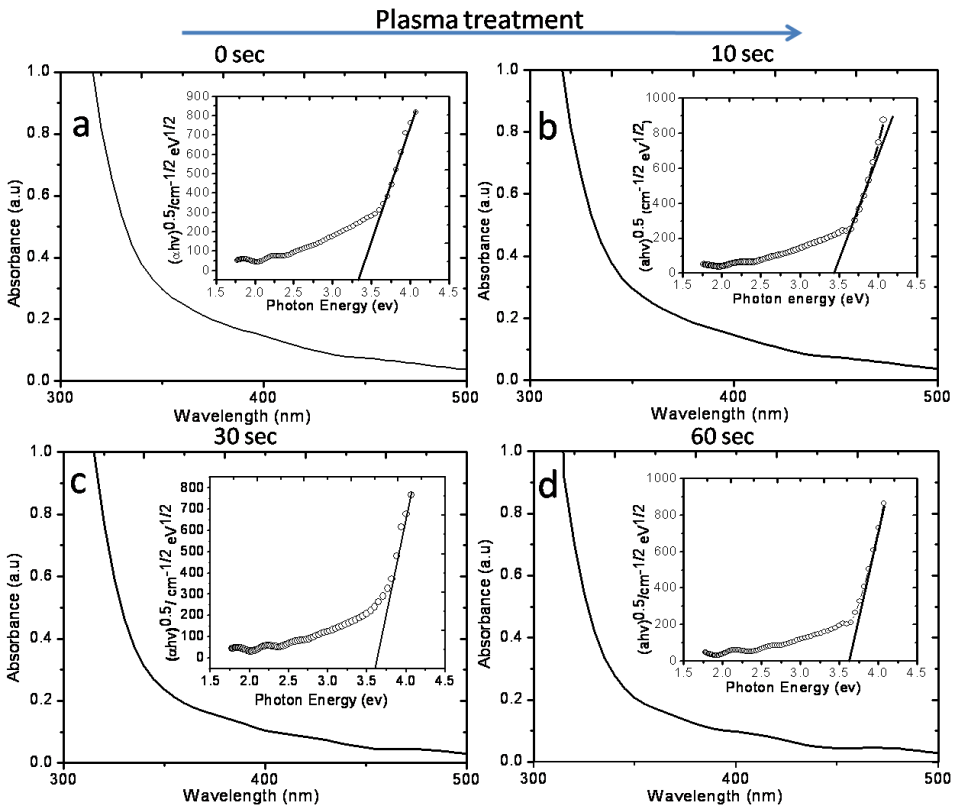

Fig.11: Optical absorption spectra and Tauc plot ($(\alpha h\nu)^{1/2}$ versus $h\nu$ plot) in the inset for (a) Co doped/untreated TiO_2 film; plasma treatment time 0 second, (b) Co doped/treated TiO_2 film; plasma treatment time 10 second, (c) Co doped/treated TiO_2 film; plasma treatment time 30 second and (d) Co doped/treated TiO_2 film; plasma treatment time 60 second.

XPS study:

The variation in the chemical state of elements 'O' and 'Ti' with plasma treatment time was analyzed in detail to correlate it with the observed variations in the band gap of the films. Fig. 12(a,b,c) show high resolution Ti 2p XPS spectrum of pure TiO_2, Fe doped TiO_2 and Co doped TiO_2 thin film. O 1s high resolution spectra are shown in Fig. 12(d,e,f). Fig. 13(a,b) shows high resolution XPS spectrum (for $Fe2p_{3/2}$) of Fe doped and plasma treated TiO_2 film. The Co doped samples after plasma treatment show adverse effect on the band gap of the doped TiO_2 film. In this case, band gap increases with the increasing treatment time as observed in optical studies. To investigate this divergent behaviour, the samples were analyzed via XPS; Fig. 14(a,b,c) show high resolution spectrumof pure TiO_2, and Co doped samples. The change in stoichiometry wasestimated by change in the peak area of relative peaks.

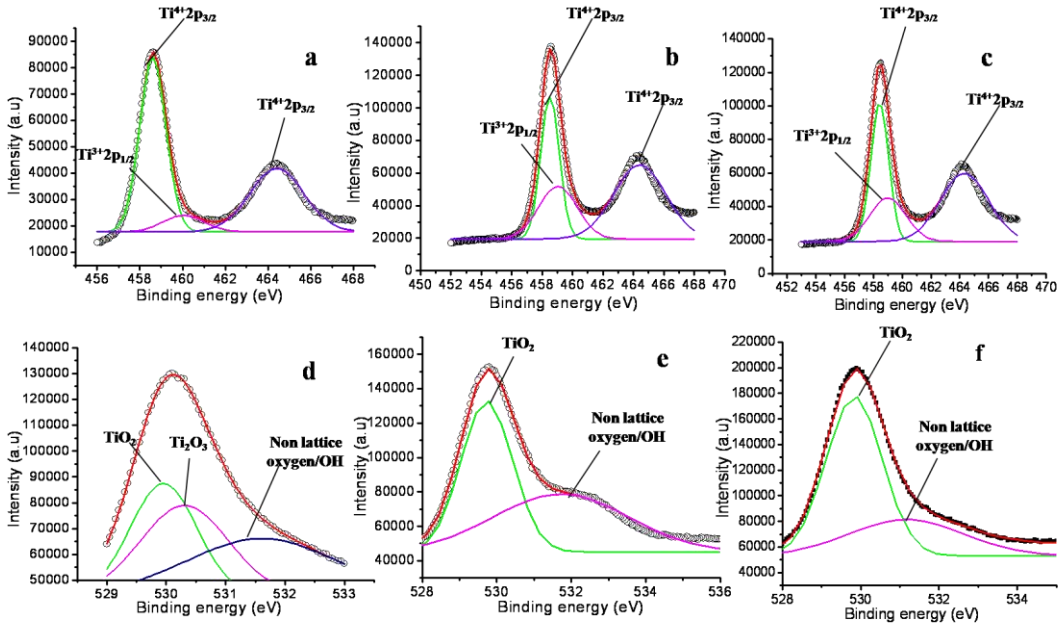

Fig.12: High resolution XPS spectra of Ti2p and O1s in (a) pure/untreated TiO_2 film, (b) Fe doped/untreated TiO_2film;plasma treatment time 0 second, (c) Fe doped/treated TiO_2 film; plasma treatment time 60 seconds, (d) O1s for pure/untreated TiO_2 film, (e) O1s for Fe doped/untreated TiO_2 film; plasma treatment time 0 second, and (f) O1s for Fe doped/treated TiO_2 film; plasma treatment time 60 seconds.

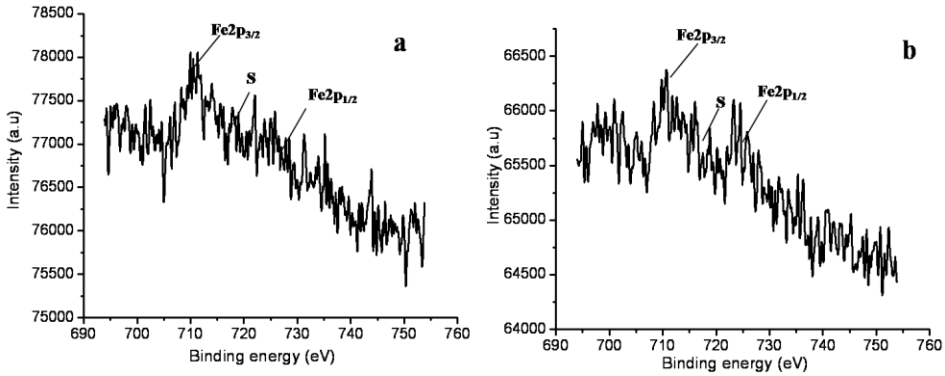

Fig.13: High resolution XPS spectra of Fe2p in (a) Fe doped/untreated TiO_2 film and (b) Fe doped/treated TiO_2 film.

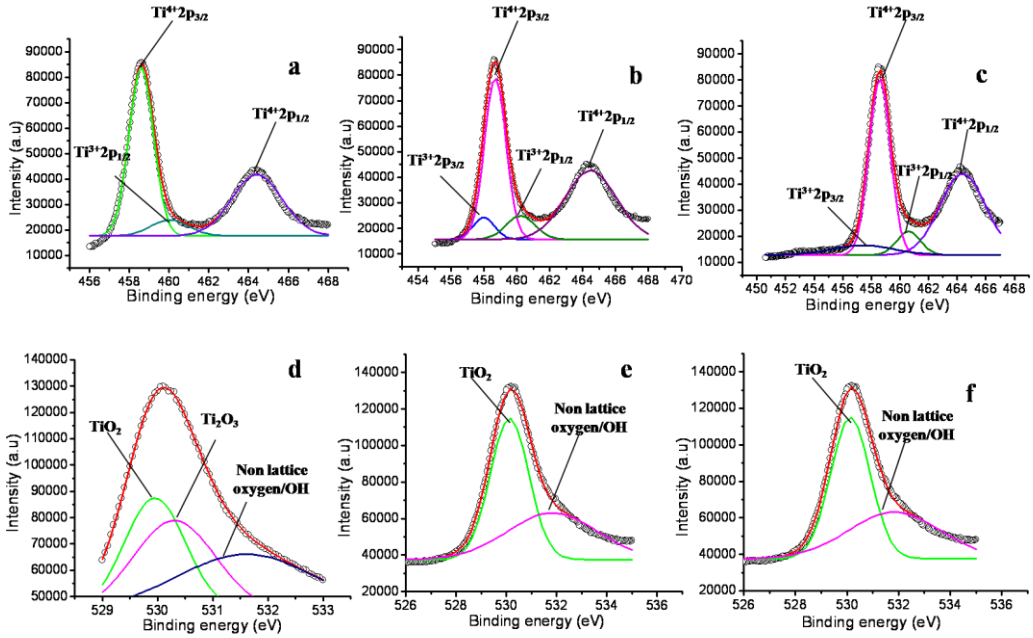

Fig.14: High resolution XPS spectra of Ti2p and O1s in (a) pure/untreated TiO_2 film, (b) Co doped/untreated TiO_2 film; plasma treatment time 0 second, (c) Co doped/treated TiO_2 film; plasma treatment time 60 seconds, (d) O1s for pure/untreated TiO_2 film, (e) O1s for Co doped/untreated TiO_2 film; plasma treatment time 0 second, and (f) O1s for Co doped/treated TiO_2 film; plasma treatment time 60 seconds.

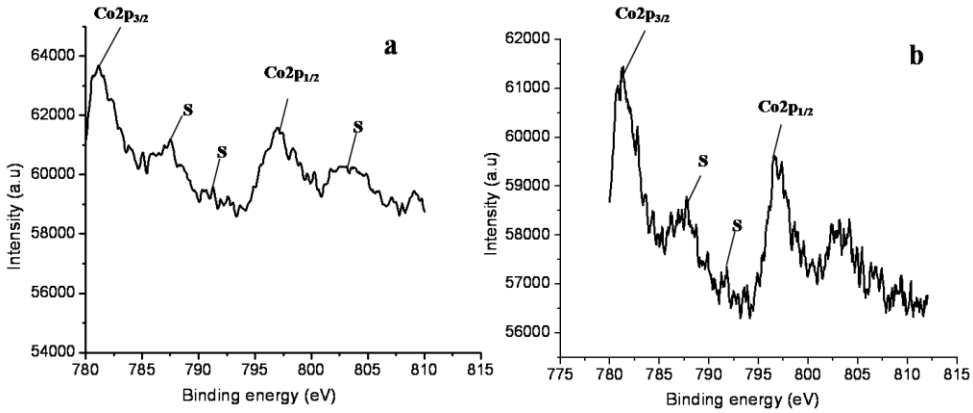

Fig.15: High resolution XPS spectra of Fe2p in (a) Co doped/untreated TiO_2 film and (b) Co doped/treated TiO_2 film.

O 1s high resolution spectra are shown in Fig. 14(d,e,f). Fig. 15(a) corresponds to high-resolution XPS spectra of Co2p region of Co doped TiO_2 thin films and Fig. 15(b) is high-resolution XPS spectra with plasma treatment. In Fe doped TiO_2 thin film, the formation of oxygen vacancies and Ti^{3+} enhance absorbance and red shift due to the formation of energy levels in the band gap, whereas in Co doped TiO_2 the Burstein-Moss shift is effective to make blue shift in the absorption spectra as shown in Fig. 16. Conclusively, we can say that the joint approaches i.e. low level/moderate doping

and safe and low cost air plasma treatment resulted in enhanced optical properties of transparent TiO_2thin films, making them efficient candidate for transparent electrode applications.

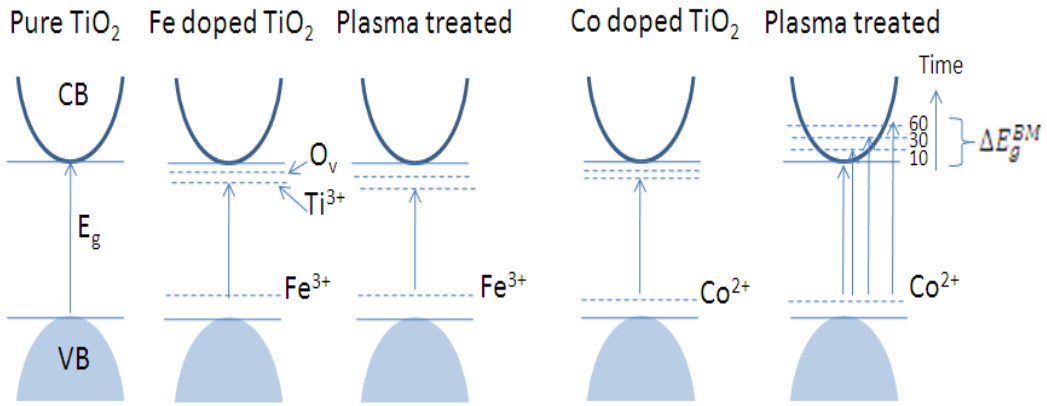

Fig.16: Schematic diagram of the energy levels of (a) pure/untreated TiO_2 films, (b) Fe doped/untreated TiO_2 film, (c) Fe doped/treated TiO_2; for 60 seconds of treatment time, (d) Co doped/untreated TiO_2 film, (e) Co doped/treated.

2.3 OBJECTIVE 3:

Structural and optical properties of undoped and transition metal doped TiO_2 thin films:

In this objective, thin transparent film of pure, Fe and Co doped TiO_2 thin films were obtained by sol-gel dip coating method. First, Fe and Co doped TiO_2 thin films were formed on glass substrate, which were annealed at 300^{o}C. Dopants were used to enhance the optical properties of thin films. Structural properties of as synthesized samples showed that the dopants in TiO_2 exhibit no tendency and/or precipitate in different phase during the synthesis process. Similarly, the obtained diffused reflectance spectra explain a shift in the visible region.

Experimental Methods:

TiO_2, Fe doped TiO_2 and Co doped TiO_2 thin films were fabricated on glass substrate using same sol-gel dip coating method as followed in the objective 2.1&2.2. The synthesis is similar to objective 2.1. Coated films were dried and annealed at 300^{o}C to form transparent thin films.The structural and optical properties of thin films were investigated.

Structural and Optical analysis of undoped, Fe and Co doped TiO_2 thin films

Fig. 17 shows the XRD pattern of pure, Fe and Co doped TiO_2 thin films. As all the synthesized samples were annealed at 300^{o}C, the major peak detected at the diffraction angle (2θ) 25.5^o

corresponds to the amorphous phase of TiO_2 [15]. No dopant impurities phase were detected. Fe^{3+} and Co^{2+} ions can be easily incorporated into the TiO_2 lattice via displacing Ti^{4+}site due to their close ionic radii.

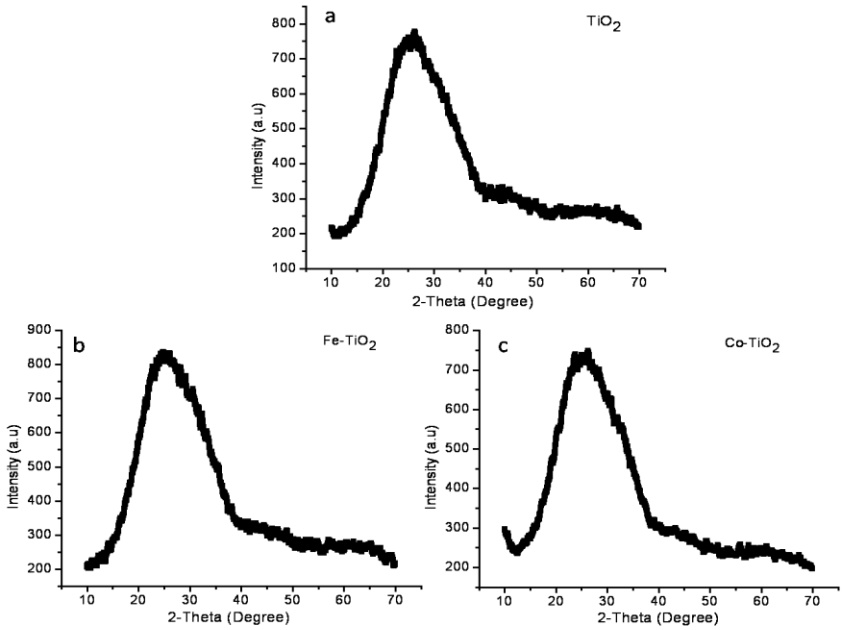

Fig.17: XRD pattern of (a) pure TiO2, (b) Fe doped TiO_2 and (c) Co doped TiO_2 thin films.

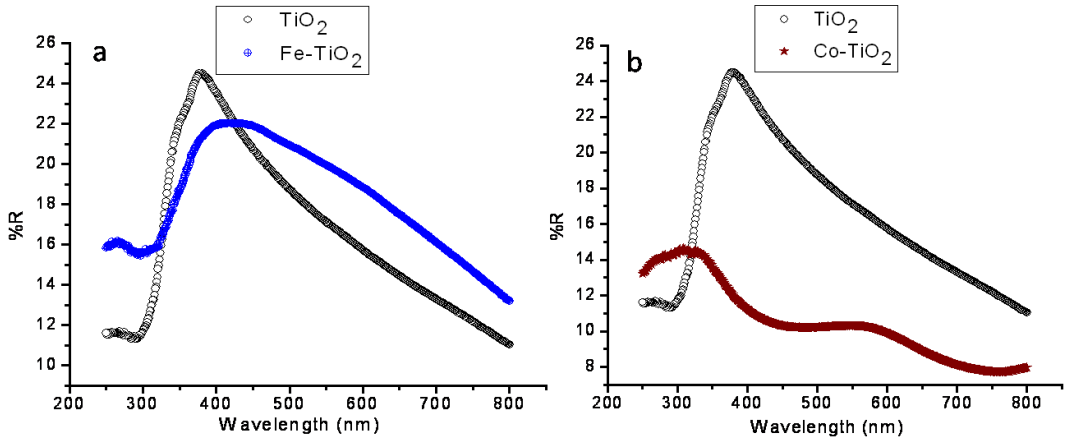

Fig.18: Diffuse reflectance of (a) TiO_2, Fe doped TiO_2 and (b) TiO_2, Co doped TiO_2 thin films.

Visible ultraviolet spectra of pure, Fe and Co doped TiO_2 thin films were obtained by diffused reflectance spectra. Fig. 18 illustrates the diffuse reflectance spectra of pure TiO_2, Fe and Co doped TiO_2 thin films on glass substrate, after heat treatment at 300^oC. The spectra of doped

samples showed a shift in the band gap transition to longer wavelength. Thus band gap narrowing can allow more absorption in the visible light and more efficient photogenrated electron transfer, the prepared samples can be expected to enhance the photocatalytic activity.

Conclusion:

We have successfully enhanced wetting and optical properties of TiO_2 thin films. The films were made by simple sol-gel method, which were treated with air plasma in DC- glow discharge exposure.

We observed that by DC-glow discharge plasma exposure a significant decrease in the contact angle of test liquids on the surface of TiO_2 thin films resulted in the enhanced surface energy which in turn enhanced the wetting property of the films

The contact angle for deionized water decreased from 54.40^o to a super wetting regime 3.02^o and similarly for ethylene glycol from 48.82^o to 1.85^o. The investigations showed that the improvement of hydrophilicity for lower exposure time in plasma is mainly due to the creation of dangling bonds/ surface defects, and higher exposure time in plasma creates nanometer scale surface roughness that enhances the surface wetting further and makes it superhydrophilic.

In the optical investigations of the TiO_2 thin films, treated with air plasma, we observed a significant change. We found that the optical absorbance as well as the band gap can be tuned with the air plasma treatment, without changing the doping concentration of samples. Therefore, unlike the other treatment methods, this approach possesses transparency of TiO_2 thin film with the alteration of optical properties. While investigated with XPS, we observed that charge separation centers i.e. oxygen vacancies and Ti^{3+}, responsible for the variation of optical properties are created with the doping of metallic Fe and Co elements; which are further enhanced by the air plasma treatment. These results can be expected to enhance the photocatalytic activity of as prepared thin films as well.

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4. Publication:

1. Bandna Bharti, Santosh Kumar, Heung-No Lee & Rajesh Kumar "Formation of oxygen vacancies and Ti^{3+} state in TiO_2 thin film and enhanced optical properties by air plasma treatment"**Scientific Reports** 6:32355 **(I.F 5.22).**
2. Bandna Bharti, Santosh Kumar & Rajesh Kumar "Superhydrophilic TiO_2 thin film by nanometer scale surface roughness and dangling bonds" **Applied Surface Science** (Vol 364, Pages 51–60, 2016) **(I.F. 3.15)**.

Publications in Proceedings:

1. Banda Bharti and Rajesh Kumar (2016).Formation of surface groups to enhance the wettability of titanium dioxide (TiO_2) thin films, International Conference on Advances in Nanomaterials and Nanotechnology (ICANN-2016) from 4-5 November 2016, organized by centre for Nanoscience and Nanotechnology, JamiaMilliaIslamia, New Dehli, India.
2. Bandna Bharti, ParthaBir Barman, Rajesh Kumar (2015). XRD analysis of Titanium Dioxide (TiO_2) and Fe doped TiO2 nanoparticles by Williamson Hall Method, 4th National conference on advanced materials and radiation physics. ***AIPProceedings*** *of the AMRP2015* [Sangroor, Punjab, India: March 13-14, 2015].

Manuscript in preparation

1. Cobalt doped TiO_2 Nano thin films: Plasma treatment, Phase Structure, Surface, and Magnetic Properties"
2. Photocatalytic activity of TiO_2 thin films-Effect of plasma treatment.